



NRL/MR/6110--17-9709

Headspace Analysis of Ammonium Nitrate

G. ASHER NEWSOME

*Nova Research, Inc.
Alexandria, Virginia*

F. LUCUS STEINKAMP

*National Research Council
Chemical Dynamics and Diagnostics Branch
Chemistry Division*

BRADEN C. GIORDANO

*Chemical Dynamics and Diagnostics Branch
Chemistry Division*

January 25, 2017

Approved for public release; distribution is unlimited.

REPORT DOCUMENTATION PAGE				Form Approved OMB No. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.					
1. REPORT DATE (DD-MM-YYYY) 25-01-2017		2. REPORT TYPE Memorandum Report		3. DATES COVERED (From - To) 14 July 2015 – 15 September 2015	
4. TITLE AND SUBTITLE Headspace Analysis of Ammonium Nitrate				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) G. Asher Newsome, ¹ F. Lucus Steinkamp, ² and Braden C. Giordano				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER 61-8906-A6	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Naval Research Laboratory, Code 6110 4555 Overlook Avenue, SW Washington, DC 20375-5320				8. PERFORMING ORGANIZATION REPORT NUMBER NRL/MR/6110--17-9709	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) U.S. Department of Homeland Security Science and Technology Directorate Homeland Security Advanced Research Projects Agency Explosives Divisions				10. SPONSOR / MONITOR'S ACRONYM(S)	
				11. SPONSOR / MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.					
13. SUPPLEMENTARY NOTES ¹ Nova Research, Inc., Alexandria, Virginia ² National Research Council, Chemistry Division					
14. ABSTRACT The explosive ammonium nitrate produces ammonia and nitric acid in the gaseous headspace above bulk solids, but the concentrations of the products have been observed to change with environmental conditions. Both species were detected in real time using ambient ionization mass spectrometry with custom-designed ion-molecule reaction techniques. Neither species was detected with sufficient sensitivity in real time to observe the influence of changing ambient atmospheric conditions on concentration in the headspace. Tungsten oxide, which absorbs both species and thermally desorbs NH ₃ and NO ₂ , was synthesized as a bulk solid and as a thin layer coating for use as a preconcentration step. Methods used with ambient ionization were adopted and modified as necessary for conventional, low-pressure chemical ionization mass spectrometry to detect pre-concentrated analyte samples in the absence of background interference. Ammonia was detected successfully, but the pre-concentrator reduced nitric acid to compounds smaller than NO ₂ , including N ₂ , that could not be detected apart from background. The methodology to accurately measure ammonia and nitric acid above bulk ammonium nitrate was resolved but lacked a sufficiently-developed tungsten oxide pre-concentrator.					
15. SUBJECT TERMS Ammonium nitrate Preconcentration Mass spectrometry					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT Unclassified Unlimited	18. NUMBER OF PAGES 28	19a. NAME OF RESPONSIBLE PERSON Braden C. Giordano
a. REPORT Unclassified Unlimited	b. ABSTRACT Unclassified Unlimited	c. THIS PAGE Unclassified Unlimited			19b. TELEPHONE NUMBER (include area code) (202) 404-6320

Table of Contents

Figures.....	iv
Executive Summary	E-1
Introduction.....	1
Instrumentation	2
Ambient Ionization and Mass Spectrometry	2
Low Pressure Chemical Ionization and Mass Spectrometry	3
Results.....	4
Ammonia Detection at Atmospheric Pressure.....	4
Nitric Acid Detection at Atmospheric Pressure.....	8
Ammonia and Nitric Acid Pre-concentration	10
Low Pressure Chemical Ionization with Pre-concentration	15
Accomplishments	18
Ammonia & nitric acid pre-concentration.....	18
Ammonia detection.....	18
Nitric acid detection	19
Conclusions.....	19
References.....	20

Figures

Figure 1. FAPA configuration with afterglow plume anterior to the mass spectrometer.....	3
Figure 2. Analyte sorbent tube mounted and interfaced with a modified GC inlet.....	4
Figure 3. Reagent ion mass spectrum for 77 ppm carbon tetrachloride in helium.....	5
Figure 4. Product ion spectrum from ion-molecule reaction of ammonia with chlorocarbon reagent ions.....	5
Figure 5. Selected ion chromatograms of ammonia adduct ions, showing background signal before introducing ammonia at 3.2 minutes.....	6
Figure 6. Growth and decay of signals from 65 weight percent AN solution: CCl_3^+ (green) and sum of analyte ammonia adduct ion signals (black).....	7
Figure 7. Background ion and reagent ion effects of oxalic acid supplied to FAPA discharge at intervals.....	9
Figure 8. Infused oxalic acid supply to front of FAPA sample tee.....	10
Figure 9. Candidate solids for analyte pre-concentration: a) tungstic acid used to produce AMT on glass beads and calcined to WO_3 , b) purchased AMT calcined to WO_3 , c) commercial tungstic acid, and d) commercial tungsten oxide.....	11
Figure 10. WO_3 solids in a fritted sampling tube at a) 20 °C, and b) ≥ 350 °C.....	12
Figure 11. Selected analyte adduct signal above background from carbon tetrachloride-doped FAPA of desorbed ammonia sampled at 60 mL/min.....	13
Figure 12. A 12 amp current applied across tungsten filament in glass sampling tube under vacuum, partially obscured by blue deposit.....	14
Figure 13. Glass sampling tubes with tungsten oxide layers calcined from different tungsten deposition times.....	15
Figure 14. Carbon tetrachloride reagent ion CI spectrum on single quadrupole MS.....	15
Figure 15. Selected ion chromatogram for m/z 98 (a) and mass spectrum at 7.12 minutes (b) from ammonia-loaded, packed sampling tube heated to 350 °C from 1.25-7.50 minutes.....	16
Figure 16. Increase in m/z 18 signal from analyte NH_4^+ and decrease in m/z 57 isobutane reagent ion from analysis of ammonia desorbed from packed tungsten oxide sampling tube.....	18

Executive Summary

The explosive ammonium nitrate produces ammonia and nitric acid in the gaseous headspace above bulk solids, but the concentrations of the products have been observed to change with environmental conditions. Both species were detected in real time using ambient ionization mass spectrometry with custom-designed ion-molecule reaction techniques. Neither species was detected with sufficient sensitivity in real time to observe the influence of changing ambient atmospheric conditions on concentration in the headspace. Tungsten oxide, which absorbs both species and thermally desorbs NH_3 and NO_2 , was synthesized as a bulk solid and as a thin layer coating for use as a preconcentration step. Methods used with ambient ionization were adopted and modified as necessary for conventional, low-pressure chemical ionization mass spectrometry to detect pre-concentrated analyte samples in the absence of background interference. Ammonia was detected successfully, but the pre-concentrator reduced nitric acid to compounds smaller than NO_2 , including N_2 , that could not be detected apart from background. The methodology to accurately measure ammonia and nitric acid above bulk ammonium nitrate was resolved but lacked a sufficiently-developed tungsten oxide pre-concentrator.

Introduction

Ammonium nitrate (AN) is an ionic salt commonly used as a fertilizer and in commercial blasting applications, but it can also be utilized as an improvised explosive device (IED) when mixed with a fuel such as fuel oil, sugar or aluminum. Extensive data has been collected regarding AN aerosols in the atmosphere. [1] Ammonia and nitric acid are in equilibrium with AN aerosols, as well as other ammonium salts, such that both species are pervasive in the environment. AN IED detection efforts are therefore complicated by the ubiquity of characteristic species. The vapor pressure of AN has been measured by numerous different methods and is approximately 1.9×10^{-8} atm [2], which translates to approximately 8 ppb ammonia and nitric acid at equilibrium. Although there is a wealth of AN data collected by the atmospheric science community, there has been minimal effort to apply this knowledge to trace vapor detection of an IED formulated with AN. It has been shown that the composition of the headspace above a bulk sample of AN can vary with atmospheric conditions, most notably humidity. [3] While organic explosive compounds such as RDX and TNT do not decompose or dissociate simply due to changing phases, reliable detection of AN IEDs requires analysis for a minimum of two vastly different chemical species (and potentially many more when considering the fuel as an additional component).

Previous research efforts have focused on quantifying and characterizing the vapor phase species present above a bulk AN sample, while minimizing background interferences. A water impinging method was used for ammonia and nitric acid collection, with all samples analyzed by ion chromatography. [3] Due to poor efficiency and sensitivity, water impinger sampling required nearly 20 hours per data point, far too much time to effectively use this method as a tool for on-line validation of AN vapor generated in a laboratory setting for sensor validation purposes. A vapor pre-concentration technique was needed to reduce the analysis time. Tungsten oxide thin films have been used for ammonia and nitric acid pre-concentration followed by thermal desorption to release ammonia and nitrogen dioxide for detection by a NOx analyzer. [4] In this research, mass spectrometry was implemented as an analysis technique for both ammonia and nitrogen dioxide. Flowing atmospheric-pressure afterglow ionization mass spectrometry was used as an ambient analysis technique to characterize vapor emanating from a bulk AN sample in real time. Tungsten oxide pre-concentration was used with low pressure chemical ionization in a detection scheme designed to be analogous to the gas

chromatography/mass spectrometry (GC/MS) systems used for validating trace vapors composed of multiple organic explosive compounds. [5,6]

Instrumentation

Ambient Ionization and Mass Spectrometry

Chemical ionization (CI) was originally developed as a less energetic alternative to electron impact (EI) ionization. Atmospheric pressure chemical ionization (APCI) uses the same principals to analyze compounds in ambient conditions and retains the advantage of lower fragmentation when compared to EI. [7] Post-plasma ionization techniques are comparatively recent modifications to APCI sources and have been used to detect explosives. [8,9,10,11] Briefly, an electrical discharge through a pure gas across an electrode gap produces a cloud of ions and electrons, and the plasma of excited-state species is flowed to an analyte at a distance from the discharge. Analyte ion fragmentation is decreased as the distance of the sample from the discharge source is increased

Flowing atmospheric pressure afterglow (FAPA) ionization, a post-plasma APCI technique, was used in this research to characterize the headspace above AN. In the FAPA ion source, a negative voltage is applied across a 5 k Ω ballast resistor to a steel pin in a hollow ceramic cell (Figure 1). Helium flows from behind the pin through the cell at 0.7-1.0 L/min and out a stainless steel capillary held at ground. A 25 mA discharge on the helium between the cathode pin and anode capillary produces metastable helium ions that ionize the analyte. The plasma afterglow exits the capillary into a Teflon tee for analyte air introduction. The end of the tee is positioned 5 mm from the heated ion inlet of the mass spectrometer. A hybrid LTQ Orbitrap XL mass spectrometer (Thermo Fisher Scientific, Waltham, MA) is used for analysis. The Orbitrap analyzer is capable of a resolving power over 100000, and the LTQ linear ion trap can scan as low as 15 m/z . Both positive and negative ions were observed from the FAPA discharge.

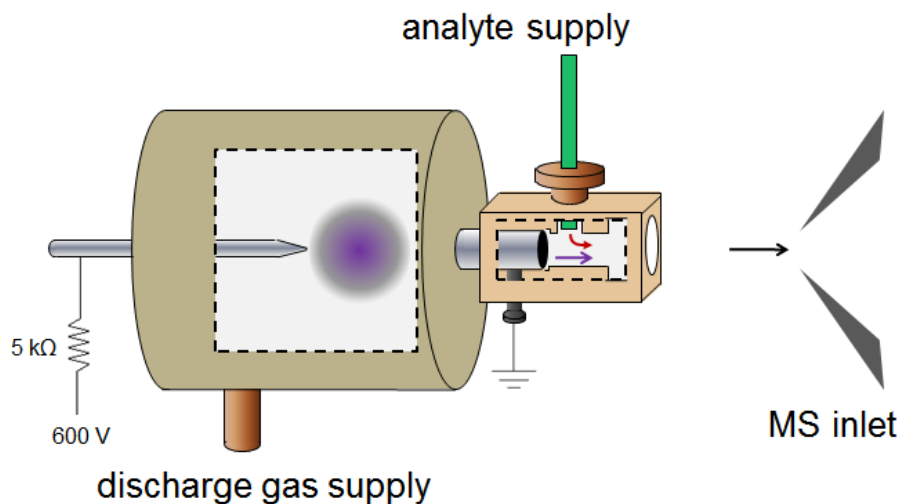


Figure 1. FAPA configuration with afterglow plume anterior to the mass spectrometer.

Post-plasma APCI sources are commonly used in positive mode to produce protonated water clusters, which in turn protonate analyte molecules. However, the protonated molecule of the analyte, ammonia, is too small for high-resolution Orbitrap analysis. Reagent gas was added to the FAPA discharge gas to promote ion-molecule reactions that generate larger ammonia adduct ions in a detectable range. [12] While a halogen-substituted hydrocarbon is effective for this purpose, such a reagent gas produces excessive charring of the ion source in an energetic discharge. Carbon tetrachloride was selected because it does not contain hydrogen and has previously been used as a low pressure CI gas for the detection of amines. [13] A specialty gas mixture of carbon tetrachloride at 500 ppm in helium was doped into the FAPA discharge gas, giving a final concentration of 25-100 ppm in helium.

Low Pressure Chemical ionization and Mass Spectrometry

Chemical ionization mechanisms employed at atmospheric pressure were reproduced with the conventional low pressure CI source of an Agilent 5975 single quadrupole mass spectrometer interfaced to an Agilent 7890 gas chromatograph (GC) (Agilent Technologies, Santa Clara, CA). Methane CI was used to optimize instrument parameters, which were checked afterward for performance with other CI gases. A 0.5 m, 0.1 μm ID glass transfer capillary was used instead of an analytical separation column due to potential reactivity with NO_2 . Analyte

from sorbent tubes was introduced to the transfer capillary either by direct interface or through connection to the independently-controlled GC pressurized inlet. The pressurized GC inlet was modified to connect directly to an analyte sorbent tube (Figure 2). Three-way valves on the sampling tube were adjusted to purge air from the tube before analysis, and helium was used to push desorbed analyte into the inlet/transfer capillary. Carbon tetrachloride was again used as a positive mode CI reagent gas, but at pressures on the order of 0.1 mTorr, as were CF_2Cl_2 , CF_3Cl , methane, and isobutane.

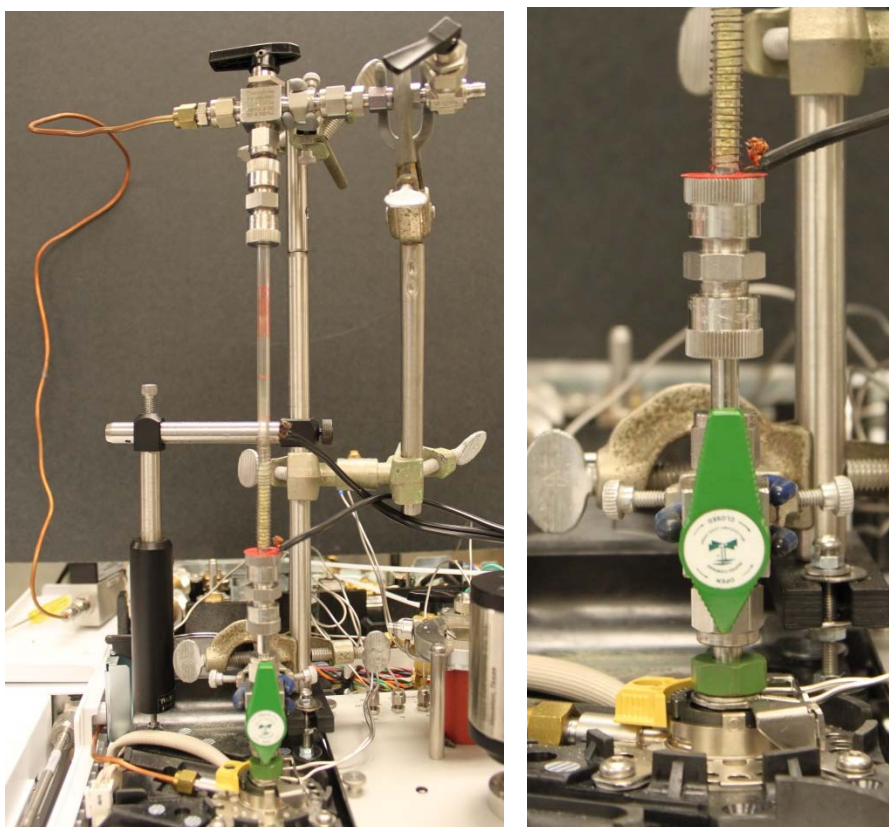


Figure 2. Analyte sorbent tube mounted and interfaced with a modified GC inlet.

Results

Ammonia Detection at Atmospheric Pressure

Carbon tetrachloride doped into the FAPA discharge produced abundant signal from CCl_3^+ and lower signal abundances from other chlorinated organic ions (Figure 3). Ammonia in

ambient atmospheric conditions reacted with carbochloride ions to produce low abundances of nitrogenated, chlorinated ions. To simulate the presence of ammonium nitrate headspace, 1000 ppm ammonia mixed in helium was supplied to the nozzle tee. A variety of analyte adduct ions were observed (Figure 4), including $[\text{CCl}_3+\text{NH}_3-\text{HCl}]^+$. The identities of the observed ions were confirmed by accurate mass measurement with the Orbitrap and MS/MS. The abundance of analyte adduct ions increased significantly above background levels at the introduction of ammonia with a corresponding decrease in the abundance of reagent ions (Figure 5).

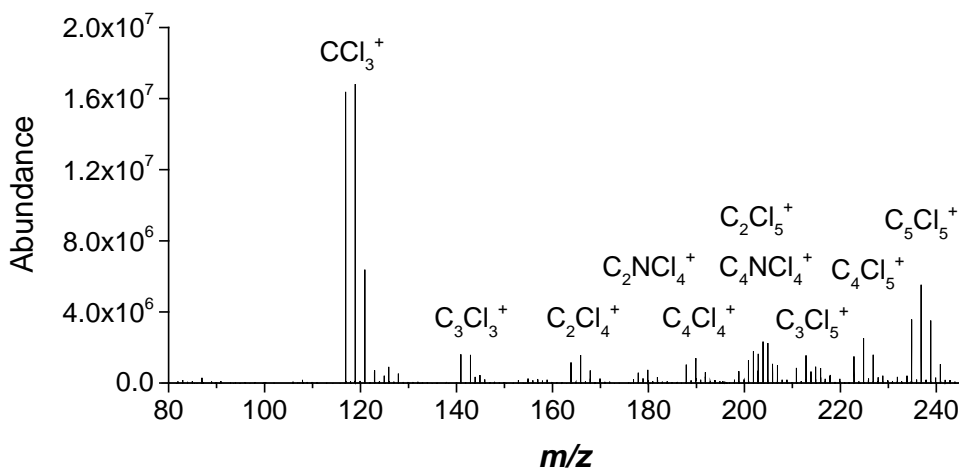


Figure 3. Reagent ion mass spectrum for 77 ppm carbon tetrachloride in helium.

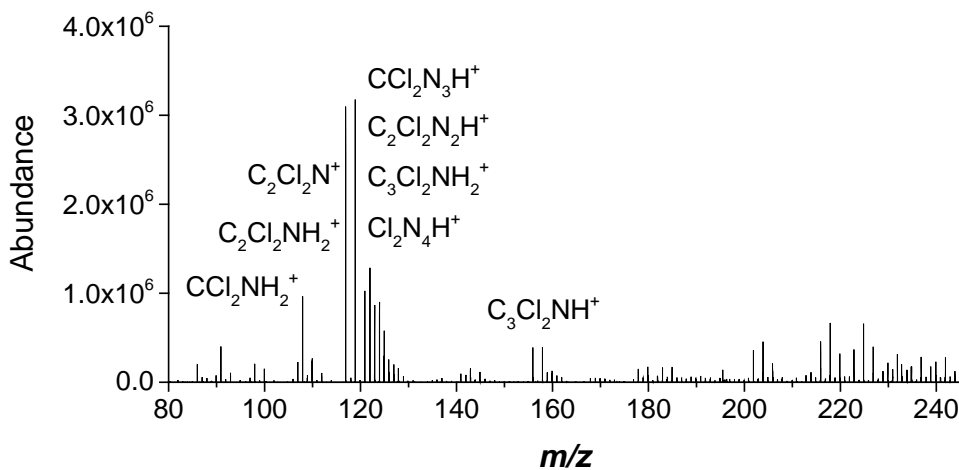


Figure 4. Product ion spectrum from ion-molecule reaction of ammonia with chlorocarbon reagent ions.

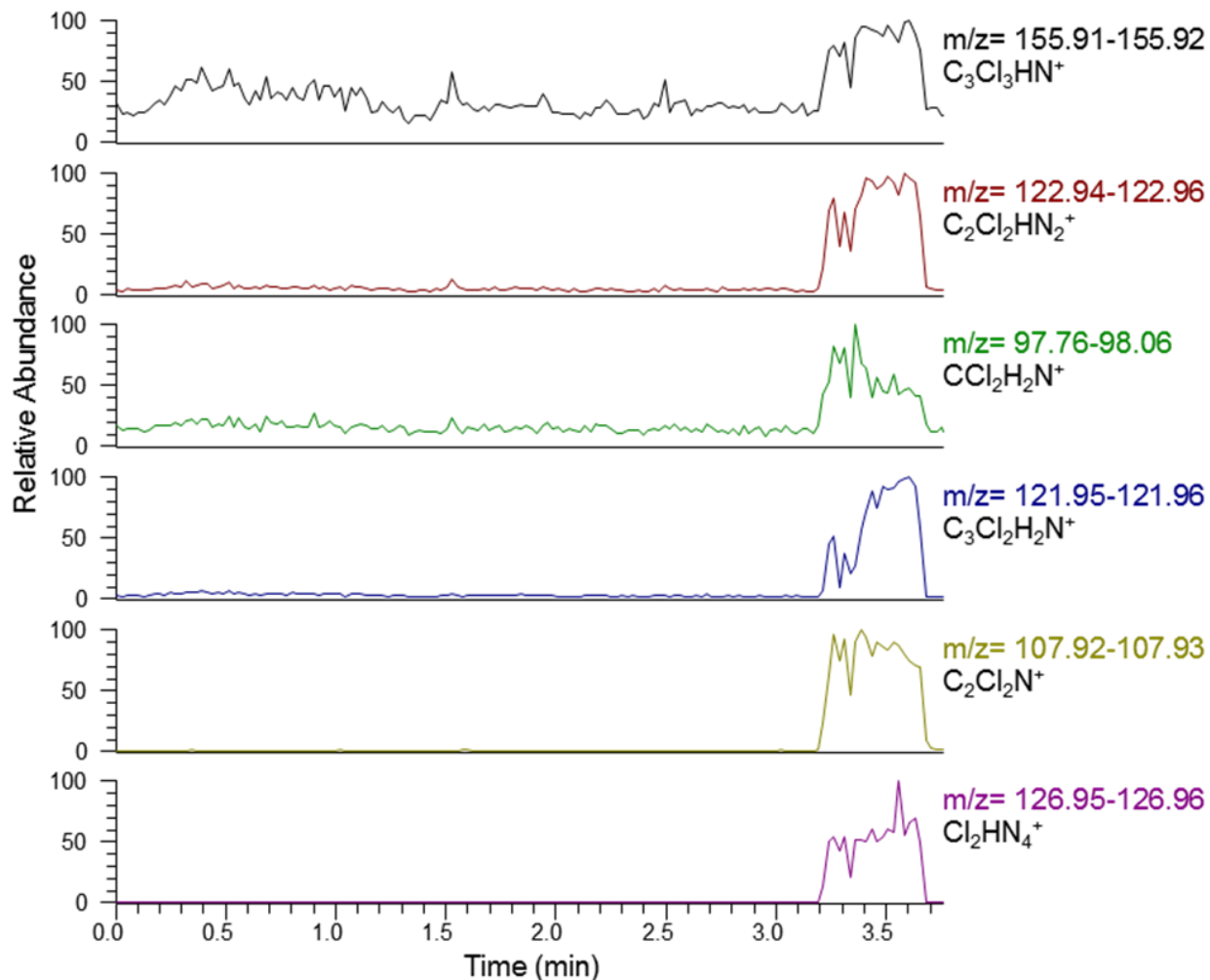


Figure 5. Selected ion chromatograms of ammonia adduct ions, showing background signal before introducing ammonia at 3.2 minutes.

Lower concentrations of ammonia were produced from AN. AN was dissolved in water to produce solutions from 10-65 weight percent. Filtered air at 9 % relative humidity (RH) was bubbled through solutions to produce ammonia in the headspace, which was routed to the afterglow via the sampling tee. Significant ammonia adduct ion signal was observed at flow rates of at least 200 mL/min. Signal remained constant for several minutes before the system became fouled with ion burn at the sampling tee and on the discharge pin (Figure 6). Analyte and reagent ion signal gradually decreased, and larger chlorocarbon ions (which were not

observed to react with ammonia) increased in abundance. Ionization was subsequently limited to two-minute analysis pulses to slow the accumulation of fouling effects.

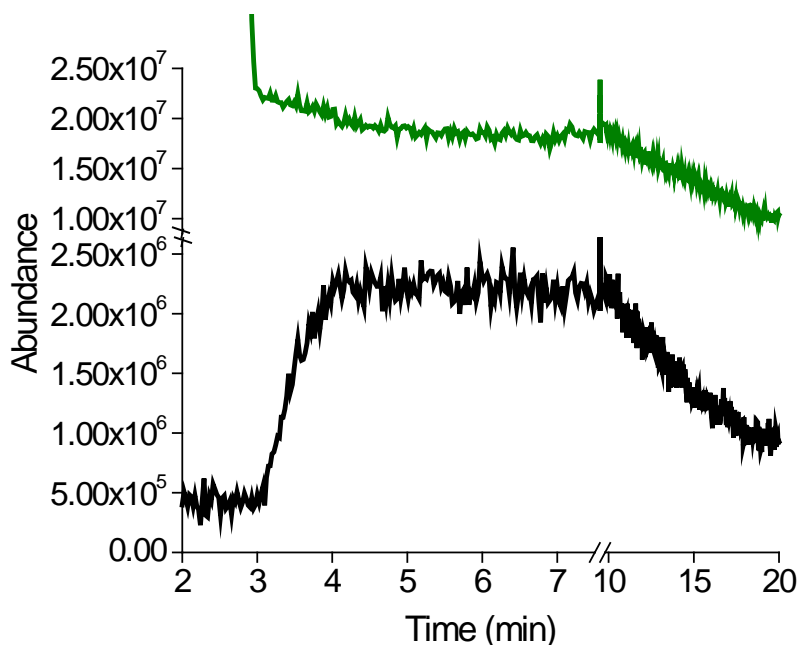


Figure 6. Growth and decay of signals from 65 weight percent AN solution: CCl_3^+ (green) and sum of analyte ammonia adduct ion signals (black).

Filtered air was flowed at 200 mL/min over 3.25 g AN solid in a 31.8 mL cell. The resulting ammonia adduct signal abundance was one tenth that of bubbled solutions. Summed analyte signal was reduced by the disappearance of some analyte ions below the detection threshold. To test atmospheric effects on headspace, air at 83% RH was flowed over solids in comparison to air at 9 % RH . No significant difference in ammonia abundance was observed from analysis times on the order of minutes.

Ion signals from multiply-chlorinated ammonia adducts were divided into isotope peaks. To increase ammonia adduct signal abundance and resolve the expected difference in ammonia concentration due to humidity effects, [3] carbon tetrafluoride was substituted for carbon tetrachloride. Monoisotopic CF_4 was added to the FAPA discharge gas, in hopes that similar chemical processes would produce ammonia adducts with integrated, more abundant ion signals. Discharge on various concentrations of CF_4 produced a series of oxygenated ions as the afterglow was exposed to air before the MS inlet, including $[\text{C}_3\text{OF}_2]^+$, $[\text{C}_4\text{H}_2\text{O}_2\text{F}_2]^+$, $[\text{C}_3\text{O}_9\text{F}]^+$,

$[\text{C}_2\text{H}_6\text{O}_6]^+$, $[\text{C}_2\text{H}_4\text{O}_5]^+$, and $[\text{C}_3\text{O}_9\text{F}+n\text{HF}]^+$. No ammonia adduct nor any meaningful decrease in the oxygenated ion abundance were observed from the introduction of high ammonia concentrations from AN solutions.

Nitric Acid Detection at Atmospheric Pressure

FAPA ionization produced a negative mode ion signal from nitrate without reagent added to the helium discharge gas. The NO_3^- signal at m/z 62 was a large and constant background signal in the absence of additional nitric acid sources because it is intrinsically formed by the atmospheric pressure discharge. [14] Background signal amplitude was also observed to vary depending on sample air flow rate to the FAPA tee. No increase in nitrate signal above background could be observed from the vapor of bubbling AN solutions or 30% nitric acid at various flow rates.

An ion-molecule reaction was introduced to selectively eliminate the background peroxy isomer of nitrate produced by atmospheric discharges. Oxalic acid, a neutral organic acid, was infused into the afterglow to bind the peroxy isomer of the nitrate ion, effectively removing it. The remaining nitrate signal can be assigned to the trigonal planar isomer of NO_3^- that is produced by HNO_3 stemming from AN dissociation. [15] With the FAPA discharge sampling only ambient air, the LTQ analyzer was used to scan for low mass ions below m/z 50. Oxalic acid was periodically deposited on paper mounted in front of the FAPA sampling tee. A subsequent background amplitude reduction of at least two orders of magnitude was observed for NO_3^- and NO_2^- , a product of nitrate fragmentation (Figure 7). Brief spikes in the background and dips in oxalic acid signal were observed at the time of each oxalic acid deposition as un-dried solvent impeded the ion-molecule reaction. Gradual increase in background signal over the total run time was observed in spite of reagent addition.

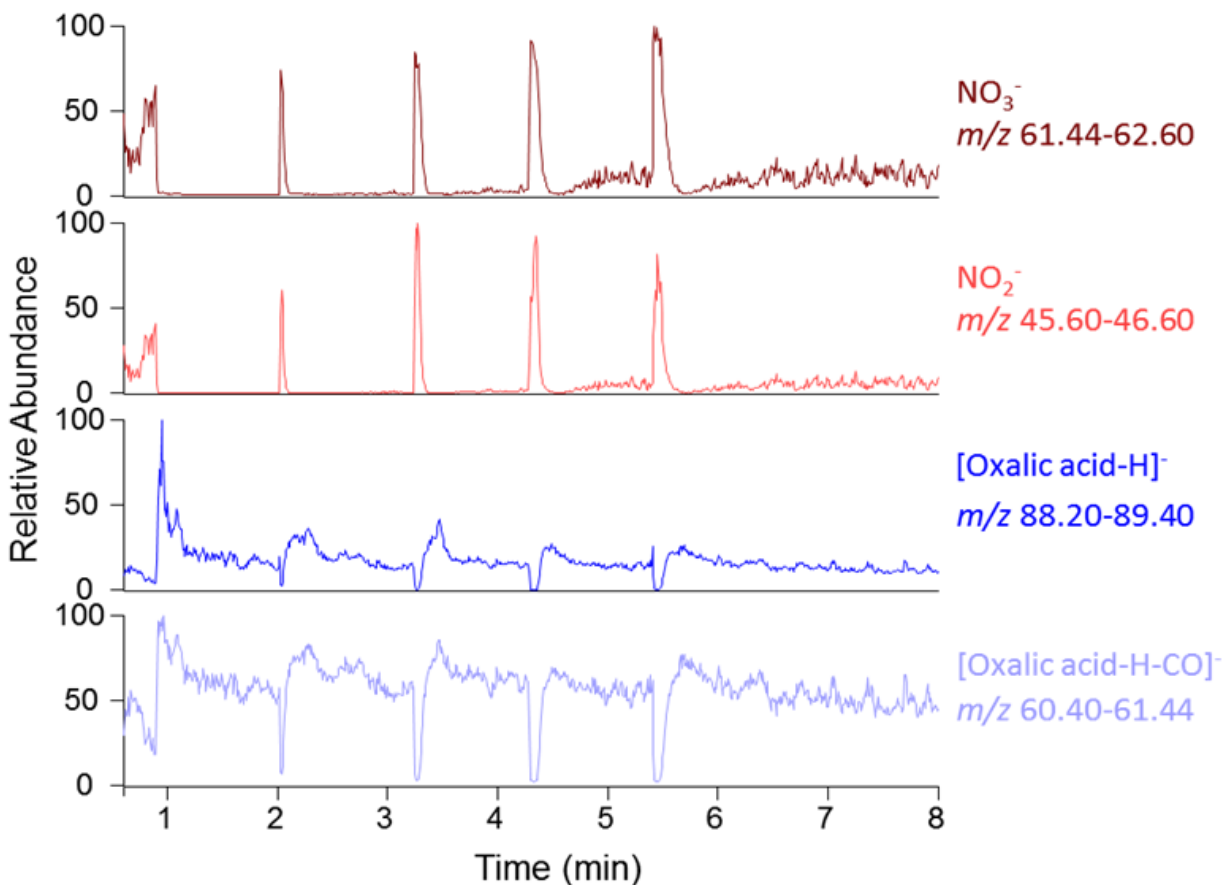


Figure 7. Background ion and reagent ion effects of oxalic acid supplied to FAPA discharge at intervals.

A reliable method for oxalic acid introduction was designed to reduce nitrate background. An electrospray needle was grounded and positioned directly in front of the FAPA sample tee (Figure 8). A solution of 0.1 g/mL oxalic acid in 75:25 methanol:water was infused through the needle, and droplets were continuously dried on the end of the needle by the hot afterglow. Oxalic acid signal and NO_3^- signal reduction were decreased if a large droplet was suspended for any length of time from the needle. Background signal was reduced at least two orders of magnitude with 15 % relative standard deviation.

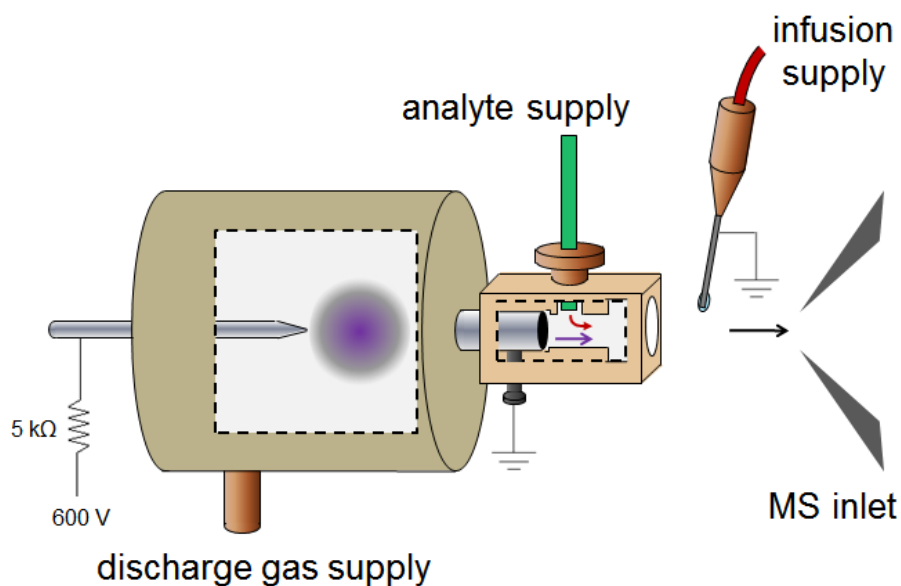


Figure 8. Infused oxalic acid supply to front of FAPA sample tee.

Both with and without oxalic acid infusion, air flow rate through the sample tee to the afterglow was observed to strongly affect signal. A switching valve was used to supply a continuous flow of either filtered air or experimental nitric acid vapor sources so that analyte signal could be measured directly opposite background. With oxalic acid infusion to knock out peroxy NO_3^- , elevated nitrate and nitrite signals over background were observed by bubbling air through 30 % nitric acid and 65 weight % AN solutions. Nitric acid signal from AN solution was particularly low. No signal from nitric acid produced by flowing air over AN solids was observable in real time, likely due to it being an order of magnitude less concentrated.

Ammonia and Nitric Acid Pre-concentration

Although the sensitivity of atmospheric pressure analysis was too low to resolve humidity effects on AN decomposition, the proof-of-principle experiments warranted adaptation of the technique to the GC-MS systems used to detect other explosives as part of the Trace Explosives Sensor Testbed program, e.g., RDX and TNT. [5,6,16] To increase sensitivity, a pre-concentration step must be added to the method. Solid tungsten oxide (WO_3) absorbs ammonia and nitric acid at room temperature and has been used as a sensor for both gases. [4,17,18] In practice, the solid oxide may hydrolyze to tungstic acid (H_2WO_4). At 350 °C the yellowish solid turns orange, desorbing ammonia while simultaneously reducing nitric acid to NO_2 vapor.

Tungsten oxide was applied as a reversible sorbent. Tungsten was resistively evaporated onto glass tubes, and tungsten oxide crystals were used as packing material inside a 1/4" o.d. glass sampling tube. The tube was then implemented for analyte adsorption, air evacuation, and analyte desorption to a low pressure CI source. Various techniques were used to synthesize WO_3 crystals as the solid packing material for thermal desorption sampling tubes. In general, a tungsten compound was crystallized on the glass surface and calcined at 500 °C in air for 2-3 hours to ensure oxidation to WO_3 . Tungstic acid was found to be moderately soluble in ammonia hydroxide and was stirred to produce ammonium tungstate in solution. Glass beads of 0.5 mm diameter were submerged in the solution and allowed to dry overnight at 60 °C. White crystals interlocking the beads formed a wafer, which became deeply yellow and brittle after calcination. Over time the WO_3 increasingly crumbled off the glass beads into powder (Figure 9a). Larger solids were produced from highly-soluble ammonium meta tungstate (AMT) (Inframat Advanced Materials, Manchester, CT) dissolved in water to make a 70% weight solution. Droplets of the AMT solution were dried at 60 °C to form white crystals of ammonium para tungstate (APT), which were calcined to chips of WO_3 (Figure 9b). The WO_3 from calcined AMT was more yellow in color than calcined tungstic acid, but both turned increasingly green over weeks of exposure to ambient air to resemble commercial tungstic acid (Sigma-Aldrich, St. Louis, MO) (Figure 9c) and commercial WO_3 powder (ESPI Metals, Ashland OR) (Figure 9d).

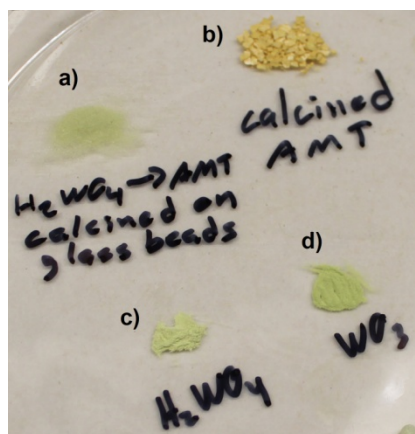


Figure 9. Candidate solids for analyte pre-concentration: a) tungstic acid used to produce AMT on glass beads and calcined to WO_3 , b) purchased AMT calcined to WO_3 , c) commercial tungstic acid, and d) commercial tungsten oxide.

The performance of each material as an ammonia pre-concentrator was tested using a Dräger ammonia sensor (Dräger Safety Inc., Sugarland, TX). The sensor was used to determine the ammonia concentration in air bubbled through an ammonium hydroxide solution. The flow of air bubbled through the solution was then passed through a sampling tube filled with the synthesized solids or a mixture of powder and sand prior to the ammonia sensor. A reduction in the sensor reading was positive proof of ammonia entrapment on the solid adsorbent. All materials were observed to absorb ammonia at room temperature, reducing sensor readings. The sample tube was wrapped with Nichrome wire and heated to 350 °C without any air flowing through the tube. The tungsten oxide turned orange (Figure 10) and a flow of clean air was passed through the tube. An increase in the ammonia sensor reading was positive proof of ammonia desorbing into the clean air stream. Results were confirmed for ammonia release from synthesized WO_3 solids using the FAPA ion-molecule reaction analysis described previously (Figure 11).

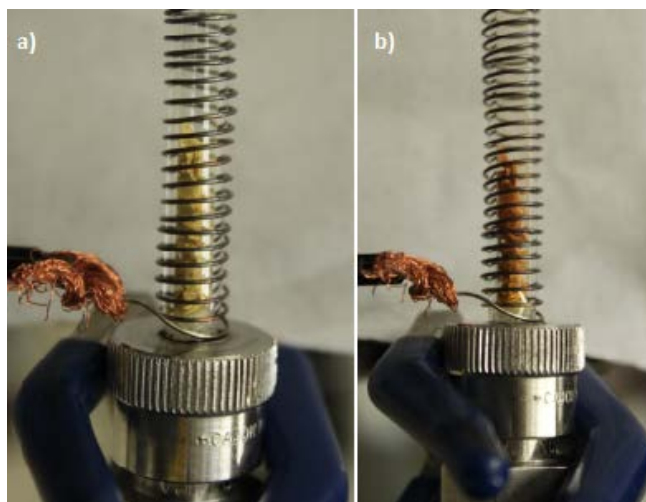


Figure 10. WO_3 solids in a fritted sampling tube at a) 20 °C, and b) ≥ 350 °C.

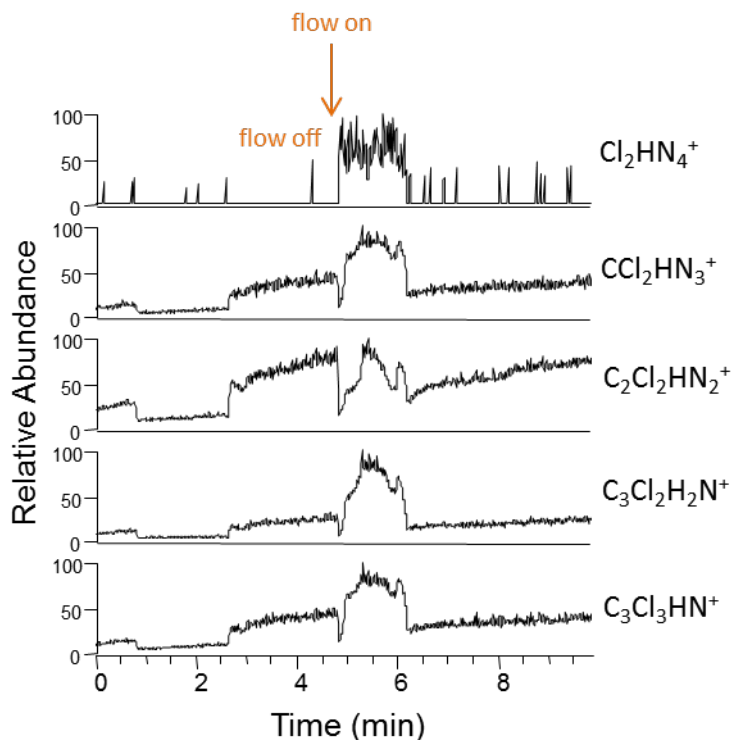


Figure 11. Selected analyte adduct signal above background from carbon tetrachloride-doped FAPA of desorbed ammonia sampled at 60 mL/min.

An evenly distributed, thin coating of WO_3 produced on the inner surface of a glass sampling tube was thought to be more conducive to generating narrow, intense signal peaks with enhanced reproducibility when compared to packed WO_3 crystals. An AMT slurry was coated and dried inside the sampling tubes but came unbound from the glass after calcination.

A resistive evaporation system was constructed to deposit polymeric tungsten oxide using a filament (12 amps) inside a sampling tube. [4] A $\frac{1}{4}$ " o.d. glass tube was held at either end by bored-through Ultratorr tee fittings. Electrical feed-throughs were produced by sealing 18 awg wire within $\frac{1}{4}$ " o.d. aluminum rods using silicone rubber. The feed-throughs were mounted in the Ultratorr fittings opposite the glass tube ends. Suspended within the tube from the leads was a straightened length of 0.020" tungsten wire. The glass tube was evacuated from both fitting tees with the pressure sensor at one end. To safely operate the circuit at 12 A, a resistor bank was constructed to divide the current drop and heat given off. Five wire-wound 25 Ω resistors were wired in parallel for a total resistance of 5 Ω . A Variac transformer was used to apply a 60 V potential with 12 A current across the tungsten filament, limiting wattage over each resistor to

144 W. An air stream was passed over the resistor bank in a fume hood to aid in cooling during operation.

Various pressures were maintained during current application, most commonly 0.50 ± 0.03 torr. Current was applied for 30 to 120 minutes, during which time the filament glowed a bright orange. Deposits from the filament produced dark banding around the glowing length, which upon cooling appeared as an almost opaque, deep blue (Figure 12). Some deposits formed unevenly, following swirling patterns that were attributed to uneven tube evacuation or vibration of a loosely-suspended filament. Deposits formed in 30 minutes were fairly thin. The most evenly-distributed deposits appeared to be attained with shorter, straighter filaments positioned at one end of the tube. Tungsten filaments became brittle and could not be reused for multiple depositions, and replicate deposits were not entirely identical.

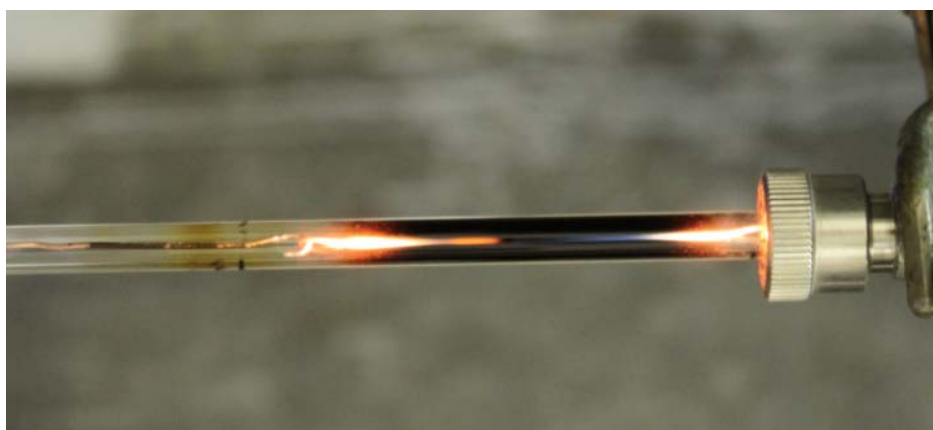


Figure 12. A 12 amp current applied across tungsten filament in glass sampling tube under vacuum, partially obscured by blue deposit.

Tungsten deposits were oxidized using Nichrome wire or a furnace. Passing air through the tube while heating to $500\text{ }^{\circ}\text{C}$ using Nichrome wire transformed the blue deposit to a pale yellow, iridescent coating with some blue spots from uneven heating. Heating the deposits in a $500\text{ }^{\circ}\text{C}$ furnace in the presence of still air produced a darker yellow but still iridescent coating (Figure 13 A). Coatings produced from filament deposits between 60 and 120 minutes appeared rough and were prone to flaking off the glass (Figure 13 B). When heated to $350\text{ }^{\circ}\text{C}$ the deposit turned orange similar to synthesized WO_3 solids, indicating successful tungsten oxide deposition.

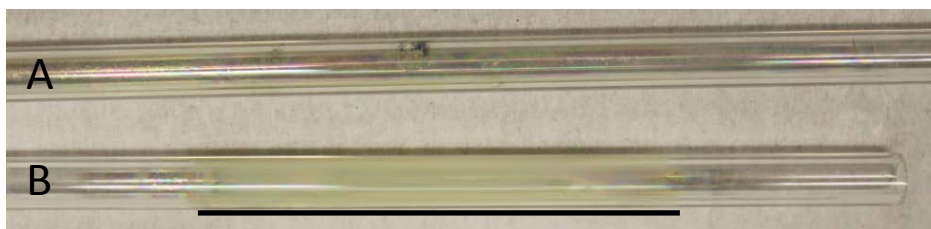


Figure 13. Glass sampling tubes with tungsten oxide layers calcined from different tungsten deposition times. A = 30 minute deposit, B = 60-120 minute deposit (line indicates region of WO_3 deposition).

Low Pressure Chemical Ionization with Pre-concentration

The ion-molecule reaction developed for FAPA detection of ammonia was adapted for low pressure CI performed without ambient background interference. Carbon tetrachloride at 500 ppm in helium was gated into the ion source as a reagent gas to produce CCl_3^+ at m/z 117, CCl_2^+ at m/z 82, and CCl^+ at m/z 47 (Figure 14). Unlike FAPA, larger chlorocarbon ions were not observed, no fouling of the ion source was evident, and signal appeared constant over many minutes.

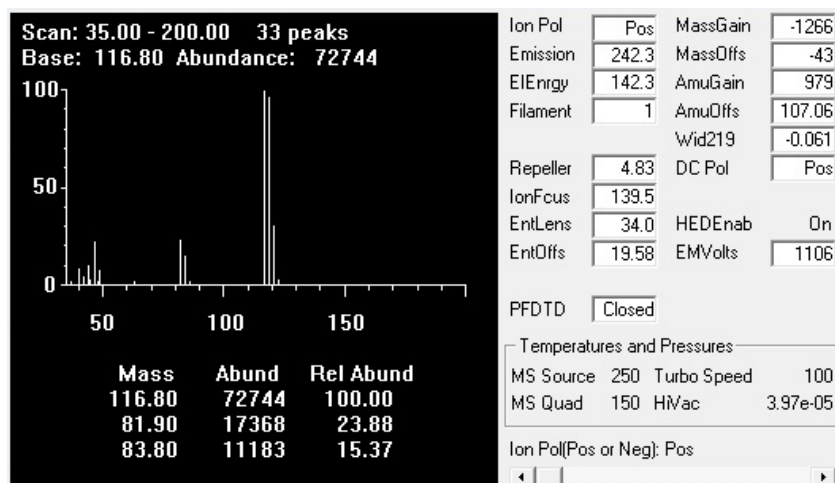


Figure 14. Carbon tetrachloride reagent ion CI spectrum on single quadrupole MS.

Air was bubbled through ammonium hydroxide to produce NH_3 vapor which was directed through a sampling tube packed with synthesized tungsten oxide solids. The sampling

tube was loaded into the system, purged with helium, and heated to ≥ 350 °C with Nichrome wire. Desorbed products were injected from the sampling tube into the transfer capillary at 5.5 mL/min while 2.5 mL/min of carbon tetrachloride CI reagent gas was supplied to the ion source. An ammonia adduct was observed at m/z 98 corresponding to $[\text{CCl}_3+\text{NH}_3\text{-HCl}]^+$ (Figure 15). The analyte ion increased from baseline, leveled off, and declined over ten minutes. Significant signal from water above background was also observed.

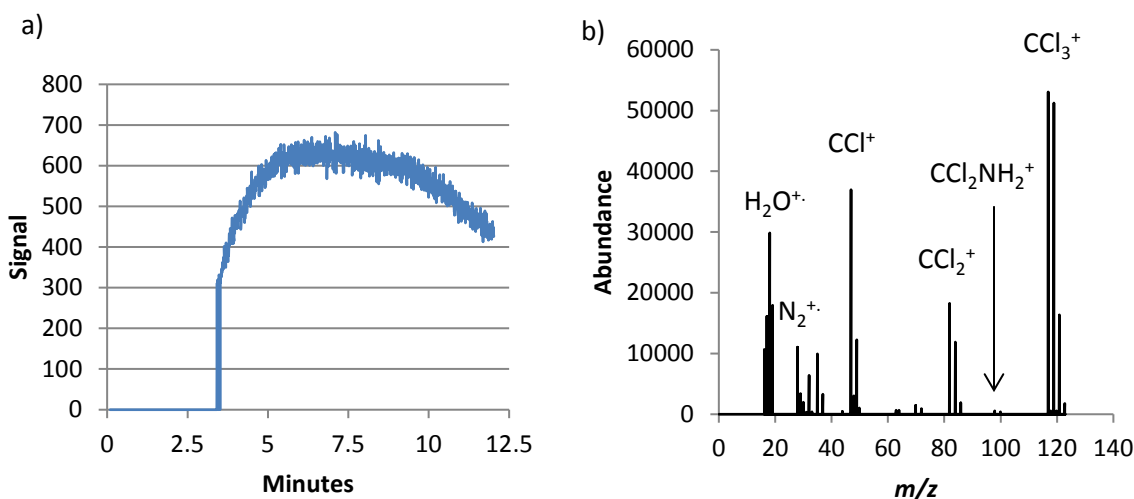


Figure 15. Selected ion chromatogram for m/z 98 (a) and mass spectrum at 7.12 minutes (b) from ammonia-loaded, packed sampling tube heated to 350 °C from 1.25-7.50 minutes.

To simultaneously reduce dead volume and control injection flow rates, the transfer capillary was connected to the pressurized GC inlet. The inlet was operated in split mode to accommodate the high flow rate of gas during injection, reducing peak tailing and increasing peak intensity. Although the ammonia analyte adduct ion was observed at m/z 98, far larger ammonia signal was observed at m/z 17, $\text{NH}_3^+\bullet$, demonstrating that CI efficiency was only about 4%. Other halogenated carbon reagent gases were tested for improved CI efficiency. The analyte adduct ion $[\text{CF}_2\text{CINH}_2]^+$ from the reaction of ammonia and CF_2Cl_2 was observed at no more than 22% abundance of m/z 17. When larger gases such as methane were mixed in significant proportion with 500 ppm carbon tetrachloride, fragmentation of the CCl_3^+ reagent ion to CCl_2^+ and CCl^+ was observed to decrease. Although the reagent ion had greater abundance, efficiency in formation of the ammonia adduct was not increased relative to $\text{NH}_3^+\bullet$.

The low efficiency of carbon tetrachloride as a reagent gas required the use of a more conventional organic CI gas to protonate analyte ammonia to NH_4^+ . Methane, the most common CI reagent gas, produced a large reagent ion peak at m/z 17 from CH_5^+ with an isotopic contribution at m/z 18. The presence of m/z 17 made it impossible to determine (at unit-mass resolution capability of the instrument) the exact efficiency of the analyte ammonia protonation. Additionally, abundant water desorbed from the packed WO_3 sampling tube contributed to the m/z 18 signal. Isobutane used as a CI reagent gas did not produce m/z 17 reagent ions and yielded complete protonation of analyte ammonia (Figure 16). Isobutane has a much closer proton affinity (678 kJ/mol) to that of water (691 kJ/mol) compared to methane (543 kJ/mol), and no water signal was observed in an analysis of products desorbed from tungsten oxide. However, isobutane was also observed to take a heavy toll on ion source filament lifetime.

The absorption of nitric acid by a packed WO_3 sampling tube was confirmed by a difference method, similar to the one used for ammonia with the Dräger sensor. Air passed through a packed WO_3 sampling tube was impinged in water for collection, and water samples were analyzed with an ion chromatograph (Dionex ICS-5000, Sunnyvale, CA). NO_2 standards were observed using negative CI mode with methane reagent and using positive mode EI, both with a 250 °C source and 150 °C quadrupole. However, NO_2 reduced from nitric acid by a packed WO_3 sampling tube could not be observed directly. Desorption from WO_3 produced abundant signals from $\text{NO}^{+\bullet}$, $\text{N}_2^{+\bullet}$, and $\text{N}_2\text{O}^{+\bullet}$, suggesting that absorbed nitric acid was reduced below NO_2 . Sampling tubes coated with WO_3 by resistive evaporation were also unable to produce NO_2 .

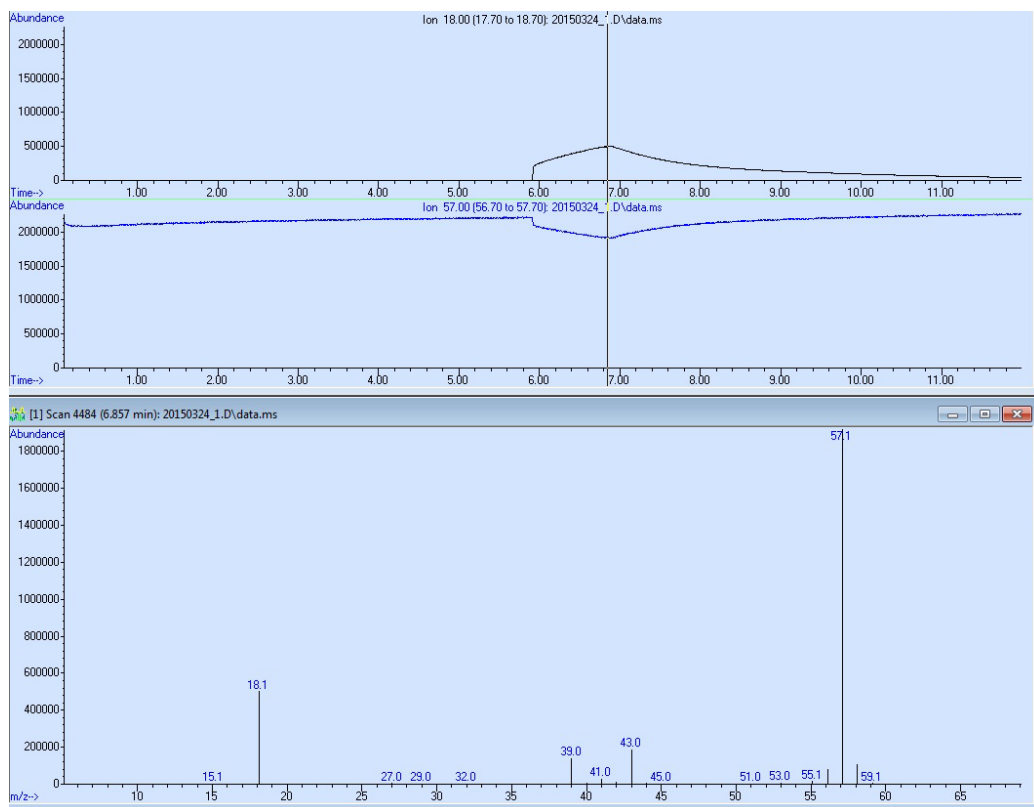


Figure 16. Increase in m/z 18 signal from analyte NH_4^+ and decrease in m/z 57 isobutane reagent ion from analysis of ammonia desorbed from packed tungsten oxide sampling tube.

Accomplishments

Ammonia & nitric acid pre-concentration

- Tungsten oxide (WO_3) can be used as an effective pre-concentration material for ammonia and nitric acid.

Note: Ammonia is desorbed from WO_3 , but HNO_3 is reduced to NO , N_2O , and N_2 .

- Bulk material can be used as packing material for a thermal desorption tube. The thermal desorption tube can be integrated into a gas chromatograph inlet for injection into a mass spectrometer.
- Tungsten can be evaporated onto the inner walls of a glass tube and oxidized to produce a thin layer of WO_3 .

Ammonia detection

- Halogenated reagent gases react with ammonia to give higher mass adducts at atmospheric pressure and at low pressure ($\sim 10^{-6}$ Torr).

Note: This process is inefficient and leaves considerable unreacted ammonia.

- Methane and isobutane efficiently protonate ammonia in low pressure CI.

Note: Methane has a reagent ion at m/z 17 making ammonia detection ambiguous.

Isobutane detrimentally shortens source filament lifetime.

Nitric acid detection

- Nitric acid can be detected at atmospheric pressure as NO_3^- but oxalic acid is needed to selectively eliminate the peroxy NO_3^- isomer generated by the ionization source.
- Nitric acid adsorbed by WO_3 , if desorbed as NO_2 , can be detected using negative mode chemical ionization with methane or isobutane.

Conclusions

The low concentrations of ammonia and nitric acid in air produced by AN dissociation and evaporation and the comparatively high ambient background of each gas prevented reliable analysis in real time. The difficulty inherent in using entirely different analysis modes and reagents for either analyte was exasperated by the added complexity of reducing background signal for nitric acid detection. An atmospheric sampling glow discharge ionization (ASGDI) source [19] would be better suited to real-time detection of ammonia using a similar ion-molecule reaction scheme. ASGDI is more appropriate for gas sampling than post-plasma probe techniques like FAPA and would likely yield greater signal abundance by limiting the number of different reagent ions. However, the technique would be subject to the same background interference from nitrate signal, require construction of a custom ion source, and be capable of sampling smaller air volumes than FAPA.

Based on strongly-established literature precedents, the pre-concentration of both ammonia and nitric acid by tungsten oxide for mass spectrometric analysis remains the most viable detection technique for simultaneous detection of both gases. Modest experimental success with producing WO_3 sampling tubes, herein, should be a positive indicator of technique viability. Collaborators more experienced in inorganic materials chemistry may be capable of producing better sampling tubes and improving synthesis such that nitric acid is properly reduced

to NO₂ by tungsten oxide or tungstic acid. Few challenges remain to the experimental design using the pre-concentrator, aside from the unperfected tungsten oxide chemistry. The current instrumental configuration requires that two WO₃ tubes must be sampled, one for ammonia and one for HNO₃, because the analytes are not separated chromatographically in a way that would allow two MS detection methods to be timed to run after a single injection. It might be possible to create a custom system in which the two gases could be effectively separated for MS analysis [20,21,22], detecting ammonia in positive mode and nitric acid in negative mode. Both MS methods would use isobutane as a reagent gas. [23,24]

A simple method to simultaneously detect ammonia and nitric acid using a single WO₃ sampling tube would be to integrate an electron capture detector (ECD) into the system. Sampling tube contents would be injected into the GC inlet, and analyte flow from the GC inlet would be split between the MS ion source and the ECD. The ECD would non-selectively detect all analytes from the sample desorption, but the MS would be used to differentiate between as many species as observable. Chemometric techniques would be used with the ECD results to derive the amount of signal actually arising from NO₂, and CI-MS would be used to quantify the ammonia.

References

1. Renard, J. J.; Calidonna, S. E.; Henley, M. V., Fate of ammonia in the atmosphere - a review for applicability to hazardous releases. *Journal of Hazardous Materials* **2004**, *108* (1-2), 29-60.
2. Ewing, R. G.; Waltman, M. J.; Atkinson, D. A.; Grate, J. W.; Hotchkiss, P. J., The vapor pressures of explosives. *Trac-Trends in Analytical Chemistry* **2013**, *42*, 35-48.
3. Steinkamp, F. L.; Giordano, B.; Collins, G.; Rose-Pehrsson, S., Volatile Emissions of Ammonium Nitrate under Flowing Conditions. *Propellants, Explosives, Pyrotechnics* **2015**, *In press*. (DOI: 10.1002/prop.201500001).
4. Braman, R. S.; Shelley, T. J.; McClenny, W. A., Tungstic acid for Pre-concentration and Determination of Gaseous and Particulate Ammonia and Nitric-Acid in Ambient Air. *Analytical Chemistry* **1982**, *54* (3), 358-364.
5. Field, C. R.; Giordano, B. C.; Rogers, D. A.; Lubrano, A. L.; Rose-Pehrsson, S. L., Characterization of thermal desorption instrumentation with a direct liquid deposition

- calibration method for trace 2,4,6-trinitrotoluene quantitation. *Journal of Chromatography A* **2012**, *1227*, 10-18.
6. Giordano, B. C.; Lubrano, A. L.; Field, C. R.; Collins, G. E., Dynamic headspace generation and quantitation of triacetone triperoxide vapor. *Journal of Chromatography A* **2014**, *1331*, 38-43.
 7. Horning, E. C.; Horning, M. G.; Carroll, D. I.; Dzidic, I.; Stillwel.Rn, New Picogram Detection System Based on A Mass-Spectrometer With an External Ionization Source at Atmospheric Pressure. *Analytical Chemistry* **1973**, *45* (6), 936-943.
 8. Cody, R. B.; Laramée, J. A.; Durst, H. D., Versatile new ion source for the analysis of materials in open air under ambient conditions. *Analytical Chemistry* **2005**, *77* (8), 2297-2302; Nilles, J. M.; Connell, T. R.; Stokes, S. T.; Durst, H. D., Explosives Detection Using Direct Analysis in Real Time (DART) Mass Spectrometry. *Propellants Explosives Pyrotechnics* **2010**, *35* (5), 446-451.
 9. Nilles, J. M.; Connell, T. R.; Durst, H. D., Quantitation of Chemical Warfare Agents Using the Direct Analysis in Real Time (DART) Technique. *Analytical Chemistry* **2009**, *81* (16), 6744-6749.
 10. Zhang, Y.; Ma, X.; Zhang, S.; Yang, C.; Ouyang, Z.; Zhang, X., Direct detection of explosives on solid surfaces by low temperature plasma desorption mass spectrometry. *Analyst* **2009**, *134* (1), 176-181.
 11. Shelley, J. T.; Wiley, J. S.; Hieftje, G. M., Ultrasensitive Ambient Mass Spectrometric Analysis with a Pin-to-Capillary Flowing Atmospheric-Pressure Afterglow Source. *Analytical Chemistry* **2011**, *83* (14).
 12. Smith, J. N.; Keil, A. D.; Noll, R. J.; Cooks, R. G., Ion/molecule reactions for detecting ammonia using miniature cylindrical ion trap mass spectrometers. *Analyst* **2011**, *136* (1), 120-127.
 13. Wang, C. Z.; Su, Y.; Wang, H. Y.; Guo, Y. L., Gas Chromatographic-Ion Trap Mass Spectrometric Analysis of Volatile Organic Compounds by Ion-Molecule Reactions Using the Electron-Deficient Reagent Ion CCl₃⁺. *Journal of the American Society for Mass Spectrometry* **2011**, *22* (10), 1839-1850.

14. Flurer, R. A.; Glish, G. L.; McLuckey, S. A., Structures of NO_3^- Formed Via Glow-Discharge in Atmospheric Gases. *Journal of the American Society for Mass Spectrometry* **1990**, *1* (3), 217-224.
15. Vilkov, A.; Cai, S.-S.; Syage, J. A., Differentiating Nitrate from Atmospheric NO_3^- by Selective Ion Molecule Reactions. In *6th Annual Workshop on Trace Explosives Detection*, Charlottesville, VA, 2014.
16. Collins, G. E.; Giordano, B. C.; Sivaprakasam, V.; Ananth, R.; Hammond, M.; Merritt, C. D.; Tucker, J. E.; Malito, M.; Eversole, J. D.; Rose-Pehrsson, S., Continuous flow, explosives vapor generator and sensor chamber. *Review of Scientific Instruments* **2014**, *85* (5).
17. McClenny, W. A.; Gailey, P. C.; Braman, R. S.; Shelley, T. J., Tungstic Acid Technique for Monitoring Nitric-Acid and Ammonia in Ambient Air. *Analytical Chemistry* **1982**, *54* (3), 365-369.
18. Llobet, E.; Molas, G.; Molinas, P.; Calderer, J.; Vilanova, X.; Brezmes, J.; Sueiras, J. E.; Correig, X., Fabrication of highly selective tungsten oxide ammonia sensors. *Journal of the Electrochemical Society* **2000**, *147* (2), 776-779.
19. McLuckey, S. A.; Glish, G. L.; Asano, K. G.; Grant, B. C., Atmospheric Sampling Glow-Discharge Ionization Source for the Determination of Trace Organic-Compounds in Ambient Air. *Analytical Chemistry* **1988**, *60* (20), 2220-2227.
20. Kolesar, E. S.; Wiseman, J. M., Interdigitated Gate Electrode Field-Effect Transistor for the Selective Detection of Nitrogen-Dioxide and Diisopropyl Methylphosphonate. *Analytical Chemistry* **1989**, *61* (21), 2355-2361.
21. Kolesar, E. S.; Reston, R. R., Silicon Micromachined Gas-Chromatography System with A Thin-Film Copper Phthalocyanine Stationary-Phase and Its Resulting Performance. *Surface & Coatings Technology* **1994**, *68*, 679-685.
22. Reston, R. R.; Kolesar, E. S., Silicon-Micromachined Gas-Chromatography System Used to Separate and Detect Ammonia and Nitrogen-Dioxide 1. Design, fabrication, and Integration of the Gas-Chromatography System. *Journal of Microelectromechanical Systems* **1994**, *3* (4), 134-146.

23. Crawford, R. W.; Coburn, T. T.; Miller, P. E.; Oh, M. S., On-line, mass spectrometric determination of ammonia from oil shale pyrolysis using isobutane chemical ionization. *American Society for Testing of Materials* **1988**.
24. Newsome, G. A.; Steinkamp, F. L., Unpublished data. 2015.

